

# Mercury and Radionuclides in Sediments of the Kaštela Bay (Croatia) – Evaluation of the Sediment Pollution History\*

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Mercury and radionuclides (natural U and its decay series products and artificial  $^{137}\text{Cs}$ ) were measured in sediments of the Kaštela Bay (eastern Adriatic coast) in the vicinity of a former chloralkali plant. The depth distributions of radionuclides and mercury revealed that sediments in front of the factory represent a mixture of natural sediment and coal ash originating from the coal used in the factory power plant. Based on this data, the hypothesis that the coal ash from the factory power plant was dumped into the sea was confirmed, and it was estimated (from  $^{137}\text{Cs}$  depth profile) that the dumping happened between 1986 and 1991. Data on the artificial radionuclide  $^{137}\text{Cs}$  was shown to be very useful for evaluation of the sediment pollution history even in such very disturbed sediments. Future monitoring of mercury pollution and radionuclides in the Kaštela Bay is suggested.

## INTRODUCTION

Mercury is one of the most hazardous environmental contaminants. Sources of mercury emission into the environment can be divided into three categories:<sup>1</sup> natural, anthropogenic and re-emitted sources (mercury remobilization from settled sources). For a long time mercury was considered to be only a local/regional contaminant, but its widespread use, as well as efficient cycling between different environmental compartments<sup>2</sup> has led to global contamination by this element, which was a key finding of the Global Mercury Assessment Report of UNEP in 2002.<sup>3</sup> Historically, chloralkali plants were major local mercury pollution sources. After it was discovered in the 1970s that mercury can be methylated in sediment<sup>4</sup> and further biomagnified in certain aquatic

food chains,<sup>2</sup> which may result in dangerously high concentrations of methyl mercury in fish, chemical plants in developed countries were mostly closed in the early 1980s. Closing mercury polluting industries in developing countries was a much slower process.<sup>1</sup> Mercury is persistent in the environment, and mercury polluted aquatic systems, in which mercury is buried in sediments, constitute long-term mercury sources.<sup>5,6</sup> For less polluted systems, natural attenuation (decrease of contamination by naturally occurring processes such as hydrodynamic flow, bioturbation, molecular diffusion, chemical transformations) may be sufficient to efficiently reduce mercury levels in contaminated aquatic systems. This process is usually very slow and a contaminated system should be regularly monitored to ensure environmental safety.

\* Dedicated to the memory of the late Professor Marko Branica.

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The most serious environmental problem of local pollution by mercury in Croatia occurred in the Kaštela Bay (central part of the Eastern Adriatic coast) following 40 years activity (1950–1990) of a chloralkali plant located on the northeastern coast of the Bay. It was estimated that at least 22 and at most 56 tons of mercury (estimated from the literature data on the range of Hg loss per ton of produced chlorine) have been altogether introduced into the bay.<sup>7,8</sup> Numerous investigations<sup>9–13</sup> have demonstrated elevated mercury concentrations in sediments and substantial bioaccumulation of total and methyl mercury in marine organisms (fish, shellfish, plankton) of this area.<sup>9,12</sup> Efficient transport of mercury from the point source of pollution is evident from the elevated mercury levels in sediments of the entire bay (0.1–10 mg/kg),<sup>9,14</sup> compared to the mercury level in sediment of the open Adriatic Sea (0.1 mg/kg).<sup>15</sup> A few years before the factory was closed (1985/86), an attempt to model the fate of mercury in the Bay demonstrated that the residence time of mercury in sediments was relatively short (less than 10 years), and that the majority of the mercury introduced into the Bay during 35 years of the factory operation was already dispersed to great distances from the point source.<sup>8</sup> It was suggested that the principal pathway of mercury transport was resuspension of highly contaminated sediment from the shallow part of the bay (in front of the factory) during storm events and transport of fine sediment particles (which contain most mercury) toward the entrance of the bay. However, more recent studies demonstrated very high concentrations of total mercury (up to 70 mg/kg) in sediments located in front of the factory<sup>10,16</sup> Further, it has been shown that the conditions in sediments are favorable for mercury methylation, and unusually high levels of methyl mercury (up to 50 µg/kg) were observed in these sediments.<sup>16</sup> In addition to mercury pollution, it was recently suspected that sediments of the bay are contaminated by uranium and its natural decay series radionuclide products originating from coal burning in the thermoelectric unit of the factory. The coal used in this small power

plant was naturally enriched in uranium<sup>17</sup> and the residual coal ash was deposited in the vicinity of the factory and protected with plastic foil and humus. However, recently found elevated concentrations of uranium in these coastal sediments<sup>17</sup> indicate that at one time this mixture might also have been dumped into the sea.

In order to elucidate the fate of mercury deposited in sediment and to evaluate the pollution history of these sediments, several sediment cores were sampled in front of the chloralkali plant and analyzed for mercury and radionuclide contents.

## EXPERIMENTAL

### *Sampling Area and Sediment Sampling*

The Kaštela Bay is situated in the central part of the eastern Adriatic coast (Figure 1) and represents a semi-enclosed bay with a total area of 60 km<sup>2</sup>, average depth of 23 m, and a volume of approximately 1.4 km<sup>3</sup>. In addition to the chloralkali plant (Figure 1), which was the source of mercury contamination, there are also a cement plant, an iron plant, a shipyard and an electroplating facility on the same northeaster bay coastline, making the Kaštela Bay one of the most polluted bodies of water on the eastern Adriatic coast.

Sediment cores were sampled in June 2000, February and October 2001 in front of the chloralkali plant (at a distance of about 50 m from the shore) by scuba divers. Cores were taken using short (20 cm long, 10 cm diameter) and long (45 cm long, 5 cm diameter) plastic tubes. Cores were immediately sliced under a nitrogen atmosphere into 2 cm (short cores) or 5 cm (long cores) slices; porewater from short cores was extracted by centrifugation and the residual sediment was conserved frozen until analyses. Several samples of coal ash were sampled in February 2001 at 3 different locations from the old deposits in front of the ancient factory.

### *Sediment Preparation and Analyses*

For mercury determination, a portion of sediment or coal ash was dried at room temperature and homogenized in an

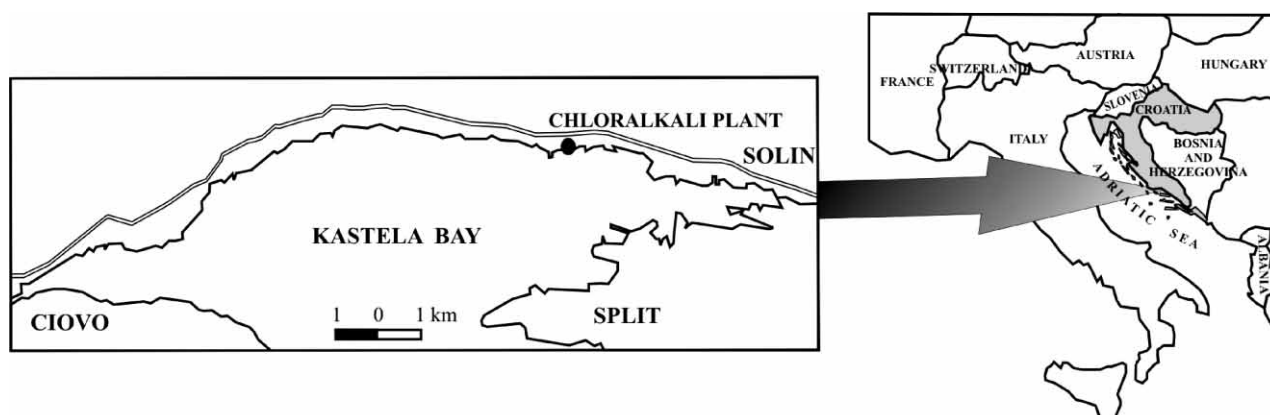


Figure 1. Location of the Kaštela Bay with the position of the former chloralkali plant.

agate mortar. About 0.2 g of sample was digested with  $\text{HNO}_3$  in a hot plate at 150 °C for 4 hours and adequately diluted for analysis. Mercury was detected by cold vapor atomic fluorescence spectroscopy (CV AFS) after  $\text{SnCl}_2$  reduction. The configuration includes a vapor generator (PSA 10.003), a gold platinum trap (PSA 10.501 Galahad) and a fluorescence detector (PSA 10.023 Merlin), and is described in detail elsewhere.<sup>16,18</sup> Organic and inorganic carbon ( $C_{\text{org}}$  and  $C_{\text{inorg}}$ ) were measured by a LECO CHNS 932 Analyzer.<sup>16</sup> After the total carbon was determined, the sediment was heated for 12 h at 400 °C to decompose organic matter so that the second determination gave values of  $C_{\text{inorg}}$ . Organic carbon values were calculated from the difference.

For radionuclide activity analysis, samples were dried at 105 °C to constant weight. Then, sediments were placed in a counting vessel of known geometry, sealed and stored for at least 4 weeks to allow ingrowth of gaseous  $^{222}\text{Rn}$ . Gamma-spectrometry measurements were performed using a HPGe semiconductor detector connected to a 8192 channel analyzer »Canberra«. Spectra were recorded for 80000 s and processed on a PC using GENIE 2K software. The  $^{137}\text{Cs}$  activity was calculated from 661.6 keV-peak,  $^{40}\text{K}$  from the 1460.7 keV-peak,  $^{226}\text{Ra}$  from the 609.3 keV-peak of its  $^{214}\text{Bi}$  progeny,  $^{228}\text{Ra}$  ( $^{232}\text{Th}$ ) from the 911.1 keV-peak of its  $^{228}\text{Ac}$  progeny, and  $^{235}\text{U}$  (after subtraction of the overlapping  $^{226}\text{Ra}$  peak) from 186 keV-peak.<sup>19,20</sup> Activities of  $^{238}\text{U}$  were calculated from the  $^{235}\text{U}$  activity assuming the  $^{235}\text{U}/^{238}\text{U}$  activity ratio of 0.04603.<sup>21</sup>

## RESULTS AND DISCUSSION

The relationship between mercury and organic and inorganic carbon is presented in Figures 2a,b. The observed negative trend ( $r = -0.558$ ,  $n = 45$ ) between mercury and

$C_{\text{org}}$  and the positive trend between mercury and  $C_{\text{inorg}}$  ( $r = 0.712$ ) are very unusual for natural sediments. In all 4 cores, correlation between Hg and  $C_{\text{org}}$  is negative, but with a variable correlation coefficient (from  $r = -0.090$  to  $r = -0.705$ ), whereas correlation between Hg and  $C_{\text{inorg}}$  is positive with highly significant correlation coefficients in all cores (from  $r = 0.735$  to  $r = 0.827$ ). Typically, positive correlation between Hg and  $C_{\text{org}}$  is found both in aquatic sediments<sup>22</sup> and in suspended matter,<sup>23</sup> as a consequence of high affinity of organic matter for complexation of mercury ion.<sup>24</sup> Lack of a relationship between Hg and  $C_{\text{org}}$  in aquatic sediments has been frequently observed as well,<sup>18</sup> but there are no examples in the literature of the negative correlation between Hg and  $C_{\text{org}}$ . Inorganic carbon in these sediments is present in the form of carbonates, which is the main component of the coarse fraction of this calcareous sediment.<sup>25</sup> A decrease in metal concentration with an increase of coarse sediment fraction (*e.g.*, carbonates) would be expected, since it is well known that metals in sediments are preferentially bound to fine particles,<sup>22,23,25</sup> whereas the coarse fraction serves as a »dilutor« of the metal concentration in unfractionated sediment. Mercury in sediments demonstrated a negative correlation with natural radionuclide  $^{226}\text{Ra}$  (Figure 3a)  $^{238}\text{U}$  (Figure 3b) and  $^{232}\text{Th}$  (Figure 3c), but a positive correlation with the artificial radionuclide  $^{137}\text{Cs}$  (Figure 3d). If we examine Hg and radionuclide depth profiles in four analyzed cores (Figure 4), we can see that in both long cores Hg and  $^{137}\text{Cs}$  demonstrate very similar depth profiles, which mirror the depth profiles of  $^{226}\text{Ra}$  and  $^{238}\text{U}$ . These profiles match the obtained positive/negative correlations between Hg and radionuclides when all samples are taken into account. Obtained correlations are less sup-

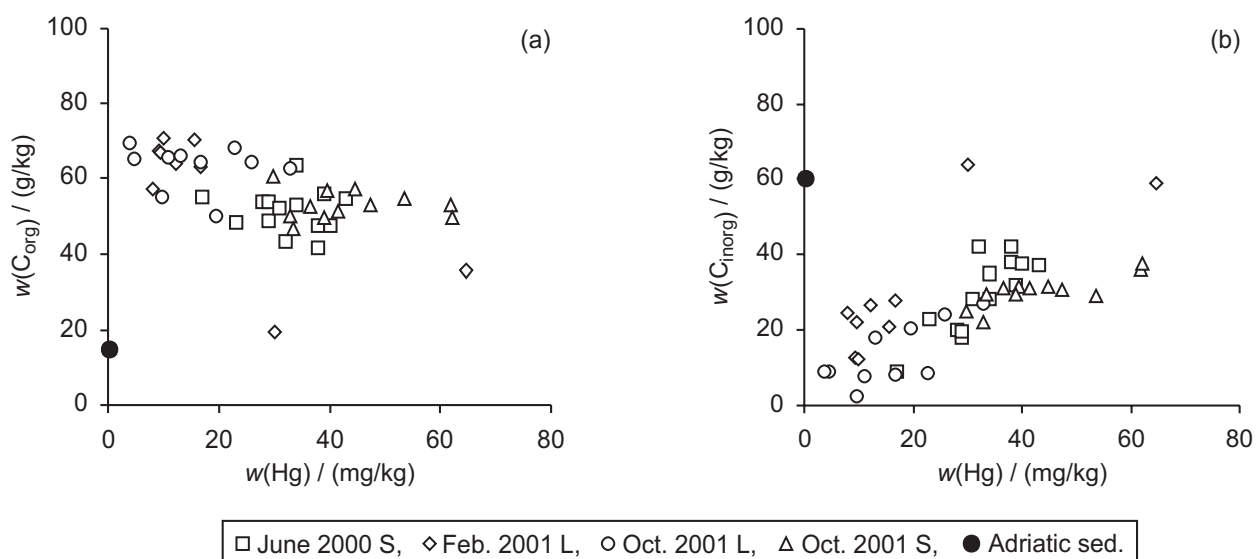


Figure 2. Relationship between mercury and a) organic carbon ( $C_{\text{org}}$ ) and b) inorganic carbon ( $C_{\text{inorg}}$ ) in sediments sampled in front of the chloralkali plant. (Mass fractions,  $w$ , are given.) For comparison, typical values for sediment from the eastern Adriatic coast are also shown (data from Table I). L – long, S – short sediment cores sampled.

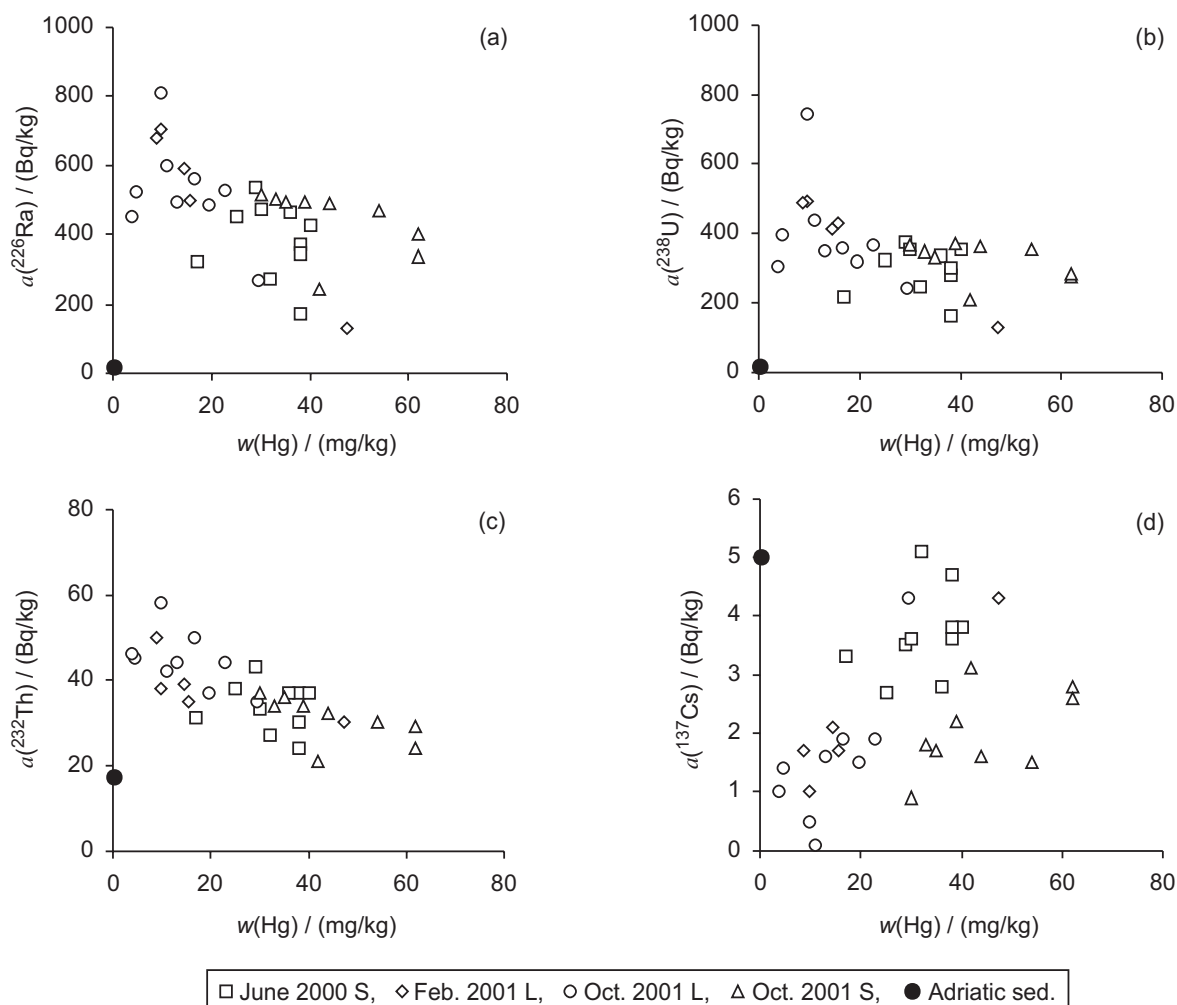


Figure 3. Relationship between mercury and natural radionuclides  $^{226}\text{Ra}$  (a) and  $^{238}\text{U}$  (b)  $^{232}\text{Th}$  (c) and artificial radionuclide  $^{137}\text{Cs}$  (d) in sediments in front of the chloralkali plant. (Mass fraction,  $w(\text{Hg})$  and specific radioactivity,  $a$ , of radionuclides are given.) For comparison, typical values for sediment from the eastern Adriatic coast are also shown (data from Table I).

ported by depth profiles found in short cores, since no obvious trends in Hg and radionuclide profiles are visible. Rather uniform depth profiles up to a sediment depth of about 20 cm could be a consequence of mechanical mixing of the surficial sediment layer by waves or by bioturbation. Cores were sampled in the shallow part of the bay at a depth of about 10 m where mixing of surface sediment during storm events is highly possi-

ble.<sup>14</sup> It was found that the sediment near the coast contains a larger fraction of coarse material (50–70 %), whereas the sediment in the center of the bay is predominantly composed of fine particles.<sup>14,25</sup> This is explained by the transport of resuspended fine sediment particles from the shallow part of the bay and their deposition under the depth of the wave base (from 10 to 20 m for the Kaštela Bay). It has actually been suggested<sup>8</sup> that

TABLE I. Ranges and average values of some parameters in coal ash and sediments from the Kaštela Bay and the eastern Adriatic coast

Sample type	$w(\text{Hg})$ (mg/kg)	$w(\text{C}_{\text{inorg}})$ (g/kg)	$w(\text{C}_{\text{org}})$ (g/kg)	$a(^{226}\text{Ra})$ (Bq/kg)	$a(^{238}\text{U})$ (Bq/kg)	$a(^{238}\text{U})$ $a(^{226}\text{Ra})$	$a(^{232}\text{Th})$ (Bq/kg)	$a(^{40}\text{K})$ (Bq/kg)	$a(^{137}\text{Cs})$ (Bq/kg)
Coal ash	1.8–22.0 8.8±12.0	12–23 17±6	37–70 49±18	820–1410 1170±315	570–860 745±155	0.64	34.0–62.0 52.5±16.0	200–250 220±30	0.8–1.0 0.9±0.1
Kaštela Bay sediment	3.8–64.8 27.6±14.5	8–64 26±12	35–87 54±6	130–810 460±145	130–750 345±110	0.76	21.0–58.0 36.5±8.0	230–370 295±30	0.5–5.1 2.4±1.2
Sediment from Adriatic coast <sup>(a)</sup>	0.1–0.4	45–90	10–20	18–22 18.5±4.0	16–23 17.6±4.3	0.95	16.8±6.5	220±120	5–10

<sup>(a)</sup> Data for the eastern Adriatic coast from Refs. 13 and 26;  $^{137}\text{Cs}$  values apply to recent sediment collected after the Chernobyl accident.

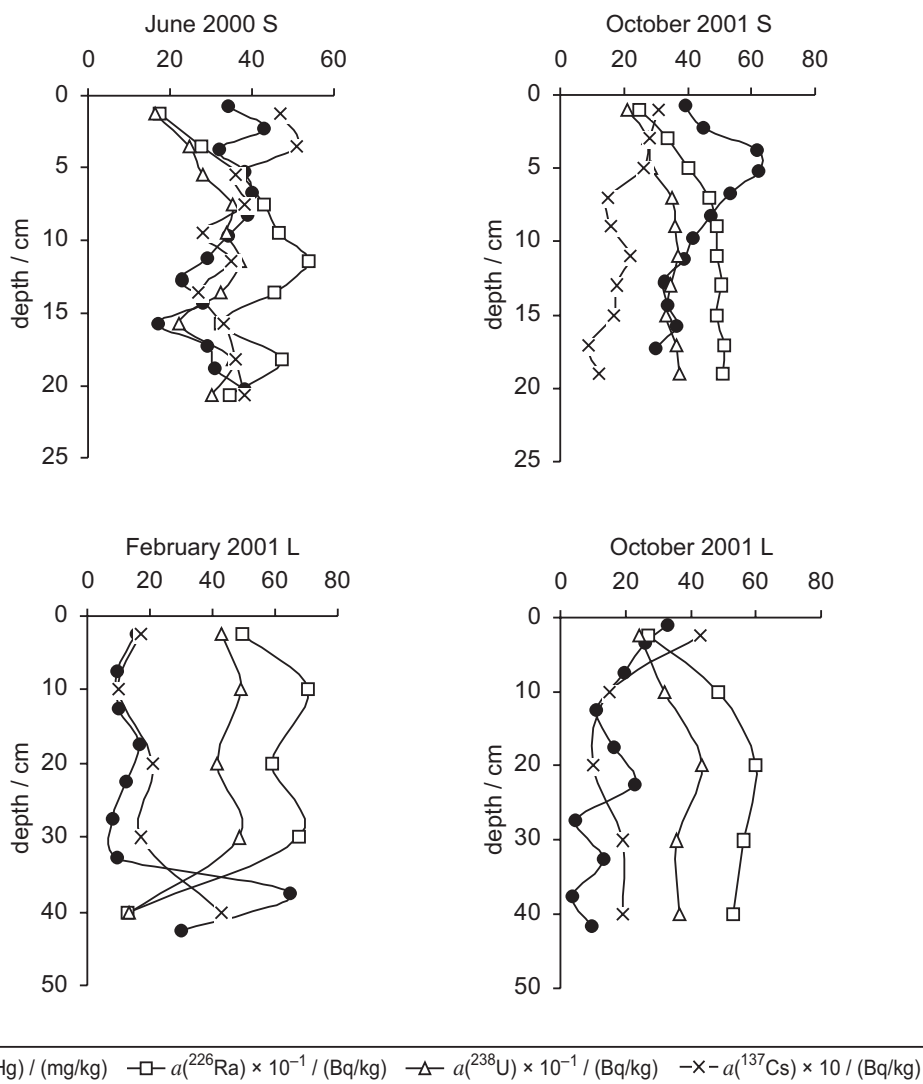


Figure 4. Depth profiles of mercury and radionuclides  $^{226}\text{Ra}$ ,  $^{238}\text{U}$  and  $^{137}\text{Cs}$  in four sediment cores sampled in front of the chloralkali plant (L – long core; S – short core).

resuspension of fine sediment particles rich in mercury, which were originally deposited in front of the chloralkali plant, and their transport by currents and waves represent the main pathway of dispersing mercury from the point source of contamination.

If we compare natural radionuclide levels measured in four analyzed cores with those in sediments from the Adriatic Sea (Figure 3 and Table I), we note that concentrations of  $^{226}\text{Ra}$  and  $^{238}\text{U}$  are on average about 20 times higher in the Kaštela Bay sediments than in sediments from the eastern Adriatic coast. Concentrations of  $^{232}\text{Th}$  are somewhat higher or similar to those in the Adriatic sediments, whereas concentrations of  $^{40}\text{K}$  are equal in the sediments of the bay and from the remaining part of the eastern Adriatic coast (for this reason  $^{40}\text{K}$  data are not presented).

(According to IUPAC the quantity used here and called "concentration" should systematically be called "mass fraction",  $w$ .)<sup>30</sup>

Our results are some of the first evidence for the contamination of recent marine sediments in the Kaštela Bay by radionuclides. More recent data (samples taken in 2004)<sup>17</sup> on the  $^{226}\text{Ra}$  and  $^{238}\text{U}$  levels in sediments taken in the vicinity of the factory (2.5 km to the left and to the right of the chloralkali plant) confirm the presence of high levels of radionuclides of the uranium decay series in sediments around the former chloralkali plant. To confirm the origin of  $^{226}\text{Ra}$  and  $^{238}\text{U}$  in these sediments, a few samples of coal ash were collected on the shore at several locations near the factory and analyzed for radionuclides, Hg and organic/inorganic carbon (Table I). Very high levels of  $^{226}\text{Ra}$  and  $^{238}\text{U}$  are evident in these coal ash samples. As mentioned above, the coal used in the factory power plant, originating from Istria, Dalmatia or Herzegovina mines, was naturally enriched in uranium. As an example, activities of  $^{226}\text{Ra}$  and  $^{238}\text{U}$  found in several coal cores collected in 1993 in one of the coal mines, used to supply the power unit in the fac-



TABLE II. Activities of  $^{232}\text{Th}$ ,  $^{226}\text{Ra}$  and  $^{238}\text{U}$  in coal cores of Tušnica region in Livanjsko polje (Bosnia and Herzegovina), sampled in 1993

S.l. <sup>(a)</sup>	Coal core depth/m	$a(^{232}\text{Th})$ (Bq/kg)	$a(^{226}\text{Ra})$ (Bq/kg)	$a(^{238}\text{U})$ (Bq/kg)	$a(^{238}\text{U})$ $a(^{226}\text{Ra})$
A	18.2–23.2	28.9	410	398	0.97
	23.5–29.4	22.7	330	424	1.28
B	21.2–26.2	6.5	584	697	1.19
	26.2–31.0	16.1	606	651	1.07
C	0.0–0.8	7.2	83	205	2.46
	1.0–1.5	7.4	147	183	1.24
D	0.0–1.0	5.0	177	179	1.01
	1.1–2.0	7.8	116	210	1.81
E	0.0–1.0	17.3	681	641	0.94
	1.0–2.0	25.9	464	451	0.97
	2.8–3.5	9.2	453	336	0.71
	3.7–4.5	10.2	482	286	0.59
	4.6–5.0	7.0	532	443	0.83
Average		13.2±8.1	390±200	392±183	1.16±0.49

<sup>(a)</sup> S.l., sampling locations.

tory, are given in Table II. It is evident that this coal contained high concentrations of  $^{226}\text{Ra}$  and  $^{238}\text{U}$ , which are, however, lower than those in the coal ash by a factor of 2–3 (Table I). Higher concentrations of radionuclides in the coal ash than in the coal are a consequence of the concentration of these elements during the burning process; they are not volatile, so they are preserved in a much smaller volume of the coal residue after burning. Concentrations of  $^{226}\text{Ra}$  and  $^{238}\text{U}$  in coal ash were on average 3 times higher, and for  $^{137}\text{Cs}$  on average 3 times lower than in the Kaštela Bay sediments. Coal ash also contains much lower concentrations of Hg (3 times

lower), and a significantly lower content of inorganic carbon, whereas levels of organic carbon are comparable in coal ash and sediment. There are therefore two types of particulate material from which sediment in front of factory is thought to be composed: coal ash, which is poor in  $\text{C}_{\text{inorg}}$ , Hg and  $^{137}\text{Cs}$  but rich in  $^{226}\text{Ra}$  and  $^{238}\text{U}$ , and coastal sediment, which is rich in  $\text{C}_{\text{inorg}}$  and Hg but poor in  $^{226}\text{Ra}$  and  $^{238}\text{U}$ . Positive correlation between Hg and  $\text{C}_{\text{inorg}}$  (Figure 2b), negative correlation between Hg and natural radionuclides (Figures 3a,b) and positive correlation between Hg and  $^{137}\text{Cs}$  (Figure 3c) all indicate that the sediment in front of the factory indeed represents a mixture of coal ash and natural sediments. If we examine Hg and radionuclide profiles (Figure 4), especially the depth profiles obtained in long cores, we can see that these two materials are mixed in a very irregular manner. In some cores an Hg maximum and a minimum of radionuclides are found at the bottom of the core (February 2001), and in others at the surface (October 2001). In an attempt to estimate the fraction of coal ash present in sediment, we calculated the percentage of coal ash from the difference in concentration of radionuclides present in coal ash and in sediment by the formula:

$$(\text{coal ash (x)}) / \% = [^{226}\text{Ra}_{(x)} - ^{226}\text{Ra}_{(o)}] / [^{226}\text{Ra}_{(\text{coal ash})}]$$

where: coal ash (x) = estimated fraction of coal ash in sediment layer x expressed in percents;  $^{226}\text{Ra}_{(x)}$  = radionuclide activity of layer x;  $^{226}\text{Ra}_{(o)}$  = average background activity of sediment from the Croatian coast (Table I), and  $^{226}\text{Ra}_{(\text{coal ash})}$  = average radionuclide activity of coal ash (Table I).

Profiles of the estimated fractions of coal ash in sediment cores are presented in Figure 5. They confirm that

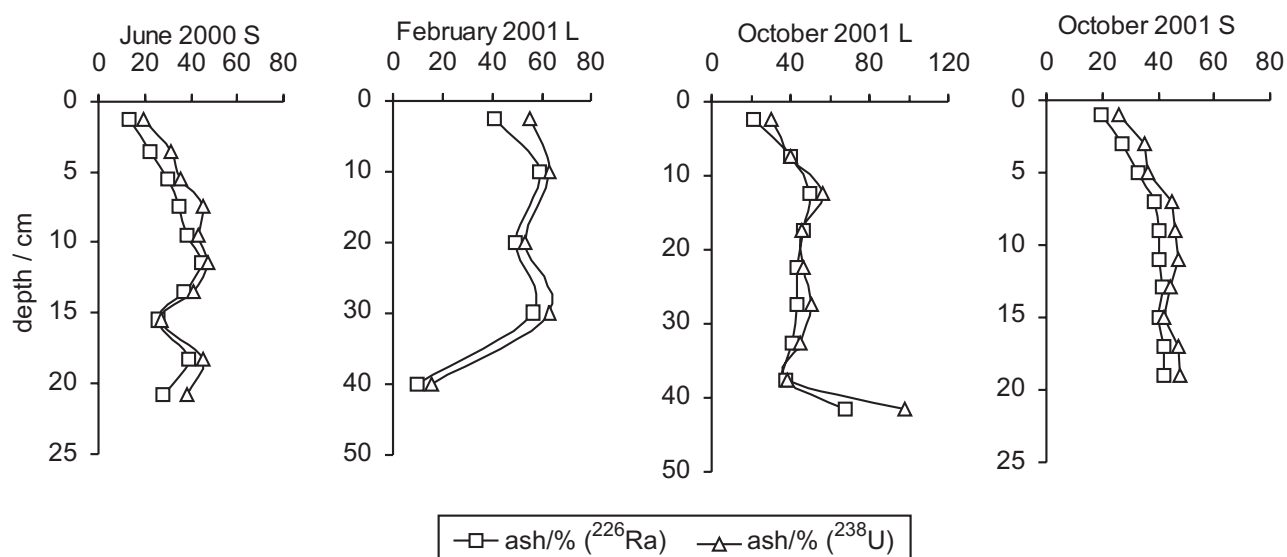


Figure 5. Coal ash mass fractions, expressed in percents, in sediments in front of the chloralkali plant calculated from the specific radioactivity of natural radionuclides  $^{226}\text{Ra}$  and  $^{238}\text{U}$ .

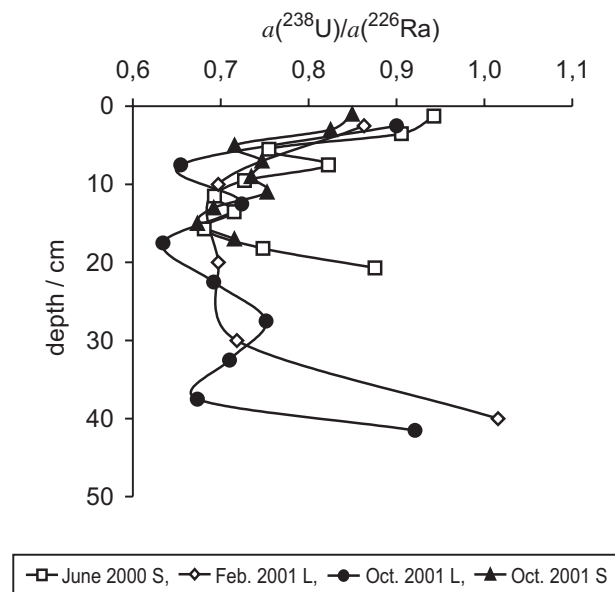


Figure 6. Depth profiles of the ratio  $^{238}\text{U} / ^{226}\text{Ra}$  in four sediment cores.

sediment and coal ash are mixed in a very irregular manner, both regarding the amount of coal ash in sediment, which varies from 15 % to almost 100 %, as well as regarding the depth distribution. In the core sampled in February 2001, coal ash is almost absent at a depth of about 50 cm, whereas in the core sampled in October 2001 at the approximately same location, the bottom of the core is composed almost entirely of coal ash. In the first 20 cm of the sediment, the fraction of coal ash is fairly constant (20–40 %) and is clearly decreasing toward the surface in the first 10 cm. Knowing that the factory was closed in 1990, and that samples were taken 10 years later (in 2000/2001), we can presume that these first 10 cm of sediment, where the radionuclide level is regularly decreasing (Figure 4), were deposited after 1990. From this assumption, we can roughly estimate the sedimentation rate at this location to be 1 cm/year. In the first 10 cm mercury decreases toward the surface in two of four cores (Figure 4), demonstrating no clear trend in diminishing mercury concentration in the sediment layer deposited after the closing of the factory. This can be most probably explained by taking into account the fact that sediment deposited even closer to the factory is much more contaminated by mercury (contains up to 200 mg/kg of Hg)<sup>16</sup> and thus still represents a continuous source of Hg for sediment deposited further away from the factory. The natural sedimentation rate in the Kaštela Bay was measured by Tudor<sup>8</sup> using sediment traps. He estimated the sedimentation rate in front of the factory (approximately at the same distance from the coast as the location where our sediment cores were taken) to range from 7–25 mm/year, the value which agrees with our estimation of 1 cm/year.

In undisturbed sediments, the concentration of  $^{137}\text{Cs}$  can be effectively used for sediment dating and for evaluation of the sediment pollution history.<sup>27,28</sup> It is known that Mediterranean sediment deposited after the Chernobyl accident (1986) contained elevated concentrations of  $^{137}\text{Cs}$ , which generally ranged between 5 and 10 Bq/kg,<sup>28</sup> whereas older sediments normally contain < 1 Bq/kg of  $^{137}\text{Cs}$ . As the Kaštela Bay sediments are obviously heavily disturbed by human activities, the mercury pollution history cannot be precisely evaluated from  $^{137}\text{Cs}$  profiles. Additionally, in the mid 1990s and later, a large amount of flyash and other soil or waste material were intensively dumped into the sea in front of the western part of the chloralkali plant. However, from the rather high concentrations of  $^{137}\text{Cs}$  in all cores, and especially from the high concentration observed at the bottom of the core sampled in February 2001 (Figure 3), we can conclude with certainty that sediments up to a depth of 50 cm were deposited after 1986. If the sedimentation rate is about 1 cm/year, 50 cm of sediment should represent the sediment deposited over the last 50 years, but according to the  $^{137}\text{Cs}$  concentrations, it represents sedimentation of less than the last 15 years. This difference agrees with the estimated fractions of coal ash in sediment (Figure 4), which suggests that at least half of the sediment at this location is composed of coal ash that was dumped into the sea between 1986 and 1991.

To get some insight into the fate of radionuclides dumped into the sediment and their impact on the ecosystem, it is interesting to examine the ratio of  $^{238}\text{U}$  and  $^{226}\text{Ra}$  (Figure 6). Depth profiles of this ratio showed that it is significantly less than 1.0 in all cores, except in the surface and bottom layers. In the original material (coal) this ratio should be about 1 (and it is exactly 1.0 if we calculate it from the average values of  $^{226}\text{Ra}$  and  $^{238}\text{U}$ , Table II). However, in the coal ash this ratio is significantly lower than 1 (Table I) and is similar to the one found in sediment. The much lower ratio in sediment and coal ash than in the coal is a consequence of the much higher solubility of uranium than radium in water (especially in seawater), which results in greater mobility of uranium compared to radium. Leaching experiments with seawater performed on the coal ash sampled in 2004 (1 g of coal ash was extracted with 10 ml of seawater for 24 h) demonstrate that up to 37 % of uranium was transferred into solution.<sup>29</sup> Lower ratios in coal ash suggest that uranium from the coal ash has been already partly leached due to regular washing of the coal ash deposited on the coast by rainwater and seawater (during stormy weather) over time. The ratio of  $^{238}\text{U}$  and  $^{226}\text{Ra}$  in natural sediment is also about 1 (Table I), so the sediments in front of the factory (which are a mixture of natural sediment and coal ash) show a higher  $^{238}\text{U}/^{226}\text{Ra}$  ratio than in the coal ash itself. Values close to 1 in the surface layer of all cores support the conclusion that the

surface layer is composed mainly of newly deposited natural material (natural sediment or flysch material) with a  $^{238}\text{U}/^{226}\text{Ra}$  ratio about 1. These data indicate that uranium in sediment is highly mobile, and that it will not stay buried in the sediment but will be transferred from the particulate to dissolved phase and further by diffusion processes to the water column, and thus to a greater distance from the source.

## CONCLUSIONS

From the data presented in this work, we conclude that sediments of the Kaštela Bay are, in addition to mercury, also contaminated with uranium and its decay series radionuclides. Until now, contamination with radionuclides was observed in the vicinity of the former chloralkali plant, which was the source of both mercury and radionuclides. Data on the artificial radionuclide  $^{137}\text{Cs}$  was shown to be very useful for the evaluation of the sediment pollution history, even in such very disturbed sediments. On the basis of Hg, U and its decay series radionuclides and  $^{137}\text{Cs}$  data, the hypothesis that the coal ash from the factory power plant was dumped into the sea was confirmed and it was estimated (from  $^{137}\text{Cs}$  depth profiles) that the dumping happened between 1986 and 1991.

The question arises of the consequences of these findings for the Kaštela Bay ecosystem, which is already considered to be one of the most endangered aquatic systems along the eastern Adriatic coast. Despite the fact that severe mercury contamination of this area was detected already decades ago, there is a lack of data about the fate of mercury in this area and especially on the transfer of toxic organic forms of mercury (methyl mercury) in the marine food chain. Data on the high mercury level in sediments even 15 years after the closing of the chloralkali plant, coupled with newly discovered contamination by natural radionuclides in the vicinity of the factory, suggest that continuous monitoring of these parameters should be carried out, as well as investigations into the distribution of mercury and radionuclides in both abiotic (water, sediment) and biotic (marine organisms) compartments in the entire bay area.

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## SAŽETAK

U sedimentu Kaštelanskog zaljeva u blizini bivše tvornice klor-alkalija (pogon elektrolize tvornice "Jugovinil") mjereni su živa i radionuklidi (prirodni uran i njegovi raspadni produkti, te umjetni radionuklid  $^{137}\text{Cs}$ ). Profili radionuklida i žive u sedimentu pokazali su da sediment ispred tvornice predstavlja smjesu prirodnog sedimenta i pepela iz ugljena koji je korišten u tvorničkoj energiji. Temeljem dobivenih podataka potvrđena je hipoteza da je pepeo iz tvorničke energije odlagan u obalno more, te je procijenjeno (iz profila  $^{137}\text{Cs}$  u sedimentu) da se to dogodilo između 1986. i 1991. godine. Pokazalo se da su podaci o  $^{137}\text{Cs}$  u sedimentu vrlo korisni za evaluaciju historijata zagađivanja sedimenta čak i u slučaju tako poremećenih sedimenata. Sugerira se praćenje stanja zagađivanja Kaštelanskog zaljeva živom i radionuklidima.